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|---|---------------------------|---|---|
| FORM PTO-1390 (REV. 11-2000) | | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | ATTORNEY'S DOCKET NUMBER |
| TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371 | | | Mo-6634/LeA 33,620 |
| | | | U.S. APPLICATION NO. (If known, see 37 CFR 1.5) |
| | | | 09/937998 |
| | | | To be Assigned |
| INTERNATIONAL APPLICATION NO. | INTERNATIONAL FILING DATE | PRIORITY DATE CLAIMED | |
| PCT/EP00/02452 | 20 March 2000 (20.03.00) | 01 April 1999 (1.04.99) | |
| TITLE OF INVENTION RUBBER COMPOSITIONS CONTAINING HYDROXYL GROUPS | | | |
| APPLICANT(S) FOR DO/EO/US 1) Thomas Scholl; 2) Jurgen Trimbach | | | |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: | | | |
| <p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p>a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> has been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>a. <input checked="" type="checkbox"/> is attached hereto.</p> <p>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p>Items 11 to 20 below concern document(s) or information included:</p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.</p> <p>14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input checked="" type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information:</p> | | | |
| PTO Form 1449 and references listed therein; Preliminary Amendment w/Abstract | | | |

1609 Rec'd PCT/PTO 27 SEP 2001

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) **09/937998** INTERNATIONAL APPLICATION NO. **PCT/EP00/02452** ATTORNEY'S DOCKET NUMBER **Mo-6634/LcA 33,620**

| | | | | | |
|---|--------------|--------------|------------|----------------------------------|--------|
| 21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a) (2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT = | | | | CALCULATIONS PTO USE ONLY | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | \$ | 860.00 |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | \$ | |
| Total claims | 5 -20 = | 0 | x \$18.00 | \$ | 0.00 |
| Independent claims | 1 -3 = | 0 | x \$80.00 | \$ | 0.00 |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) | | | + \$270.00 | \$ | 0.00 |
| TOTAL OF ABOVE CALCULATIONS = | | | | \$ | 860.00 |
| <input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. | | | | \$ | |
| SUBTOTAL = | | | | \$ | 860.00 |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | \$ | |
| TOTAL NATIONAL FEE = | | | | \$ | 860.00 |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + | | | | \$ | 0.00 |
| TOTAL FEES ENCLOSED = | | | | \$ | 860.00 |
| | | | | Amount to be refunded: | \$ |
| | | | | charged: | \$ |

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 860.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

SIGNATURE

Noland J. Cheung
NAME

39,138
REGISTRATION NUMBER

09/937998

J009 Rec'd PCT/PTO 27 SEP 2001

PATENT APPLICATION

Mo6634

LeA 33,620

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
)
THOMAS SCHOLL, ET AL) PCT/EP 00/02452
)
SERIAL NUMBER: TO BE ASSIGNED)
)
FILED: HEREWITH)
)
TITLE: RUBBER COMPOSITIONS)
CONTAINING HYDROXYL GROUPS)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Upon the granting of a Serial Number and Filing Date and prior to the examination of the subject application, kindly amend the Specification and claims as follows:

"Express Mail" mailing label number ET146899265US
Date of Deposit September 27, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D C 20231

Donna J. Yeatch

(Name of person mailing paper or fee)

Donna J. Yeatch
(Signature of person mailing paper or fee)

IN THE SPECIFICATION:

Kindly add the following abstract. A separate copy is attached.

--RUBBER COMPOSITIONS CONTAINING HYDROXYL GROUPS

ABSTRACT OF THE DISCLOSURE

The invention relates to rubber compounds that contain rubbers polymerized in solution with a secondary hydroxyl group content of 0.1 to 5 wt.-% that are not more than 4 carbon atoms away from the respective side chain end. The invention also relates to mixtures thereof with fillers, optionally additional rubbers and rubber auxiliary agents and the vulcanized rubbers produced thereof. The inventive rubber compounds are useful for producing highly reinforced, abrasion-resistant molded bodies, especially for producing tires that are characterized by excellent non-skid properties on wet surfaces.--

Kindly replace the Title of the Invention with the following:

-- RUBBER COMPOSITIONS CONTAINING HYDROXYL GROUPS --.

On page 1, line 2, kindly insert the following:

-- FIELD OF THE INVENTION --.

On page 1, line 11, kindly insert the following:

--BACKGROUND OF THE INVENTION--.

On page 2, line 23, kindly insert the following:

-- SUMMARY OF THE INVENTION --.

On page 3, line 6, kindly insert the following:

--DETAILED DESCRIPTION OF THE INVENTION--.

On page 13, before the table, kindly insert the following:

-- Table 1 --.

On page 14, before the table, kindly insert the following:

-- Table 2 --.

On page 15, before the table, kindly insert the following:

-- Table 3--.

On page 17, before the table, kindly insert the following:

-- Table 4--.

On page 18, before the table, kindly insert the following:

-- Table 5--.

IN THE CLAIMS:

Kindly cancel Claims 1 - 5.

Kindly add the following new Claims:

--6. Rubber mixtures comprising one more hydroxyl group-containing rubbers polymerized in solution and synthesized from diolefins and vinyl aromatic monomers containing bound secondary hydroxyl groups in the range of 0.1 to 5wt.%, wherein said secondary hydroxyl groups are located no further than 4 carbon atoms away from the respective side chain end.

7. Rubber mixtures according to Claim 6, wherein said hydroxyl group-containing rubber or rubbers polymerized in solution have a content of polymerized vinyl aromatic in the range of 5 to 40 wt.% and a 1,2 vinyl content in the range of 5 to 60 wt.%.

8. Rubber mixtures according to Claim 6, wherein styrene is used as a vinyl aromatic monomer.

9. Rubber mixtures according to Claim 6, wherein said diolefins are 1,3-butadiene or isoprene.

10. Molded articles containing rubber mixtures which comprise one more hydroxyl group-containing rubbers polymerized in solution and synthesized from diolefins and vinyl aromatic monomers containing bound secondary hydroxyl groups in the range of 0.1 to 5wt.%, wherein said secondary hydroxyl groups are located no further than 4 carbon atoms away from the respective side chain end.

11. A molded article according to Claim 10, wherein said molded article is a tire tread. --

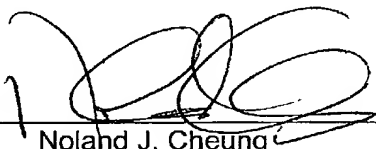
0937958-01E306

REMARKS

The Applicants respectfully request the Preliminary Amendment be entered as the amendment places the claims as well as the Specification in proper form.

New Claims 6 - 9 replace now cancelled Claims 1 - 4. New Claims 10 and 11 replaces the use claim of now cancelled Claim 5. The Applicants respectfully submit that no new matter is added.

Respectfully submitted,

By 
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Attorney for Applicants
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/jme/NJC0559

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION:

The following abstract was added. A separate copy is attached.

--RUBBER COMPOSITIONS CONTAINING HYDROXYL GROUPS

ABSTRACT OF THE DISCLOSURE

The invention relates to rubber compounds that contain rubbers polymerized in solution with a secondary hydroxyl group content of 0.1 to 5 wt.-% that are not more than 4 carbon atoms away from the respective side chain end. The invention also relates to mixtures thereof with fillers, optionally additional rubbers and rubber auxiliary agents and the vulcanized rubbers produced thereof. The inventive rubber compounds are useful for producing highly reinforced, abrasion-resistant molded bodies, especially for producing tires that are characterized by excellent non-skid properties on wet surfaces.--

The Title of the Invention has been replaced with the following:

"RUBBER COMPOSITIONS CONTAINING HYDROXYL GROUPS ~~GROUP~~
~~CONTAINING SOLUTION RUBBERS~~".

On page 1, line 2, the following was inserted:

-- FIELD OF THE INVENTION --.

On page 1, line 11, the following was inserted:

--BACKGROUND OF THE INVENTION--.

On page 2, line 23, the following was inserted:

-- SUMMARY OF THE INVENTION --.

On page 3, line 6, the following was inserted:

--DETAILED DESCRIPTION OF THE INVENTION--.

On page 13, before the table, the following was inserted:

-- Table 1 --.

On page 14, before the table, the following was inserted:

-- Table 2 --.

On page 15, before the table, the following was inserted:

-- Table 3--.

On page 17, before the table, the following was inserted:

-- Table 4--.

On page 18, before the table, the following was inserted:

-- Table 5--.

IN THE CLAIMS:

Claims 1 - 5 have been cancelled.

The following new Claims have been added:

--6. Rubber mixtures comprising one more hydroxyl group-containing rubbers polymerized in solution and synthesized from diolefins and vinyl aromatic monomers containing bound secondary hydroxyl groups in the range of 0.1 to 5wt.%, wherein said secondary hydroxyl groups are located no further than 4 carbon atoms away from the respective side chain end.

7. Rubber mixtures according to Claim 6, wherein said hydroxyl group-containing rubber or rubbers polymerized in solution have a content of polymerized vinyl aromatic in the range of 5 to 40 wt.% and a 1,2 vinyl content in the range of 5 to 60 wt.%.

8. Rubber mixtures according to Claim 6, wherein styrene is used as a vinyl aromatic monomer.

9. Rubber mixtures according to Claim 6, wherein said diolefins are 1,3-butadiene or isoprene.

10. Molded articles containing rubber mixtures which comprise one more hydroxyl group-containing rubbers polymerized in solution and synthesized from diolefins and vinyl aromatic monomers containing bound secondary hydroxyl groups in the range of 0.1 to 5wt.%, wherein said secondary hydroxyl groups are located no further than 4 carbon atoms away from the respective side chain end.

11. A molded article according to Claim 10, wherein said molded article is a tire tread. --

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Rec'd PCT/PTO 25 FEB 2002

09/937998

PATENT APPLICATION
Mo-6634
LeA 33,620

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
THOMAS SCHOLL ET AL)
SERIAL NUMBER: 09/937,998)
FILED: SEPTEMBER 27, 2001)
TITLE: RUBBER COMPOSITIONS)
CONTAINING HYDROXYL GROUPS)

SUBMISSION OF MISSING PARTS OF APPLICATION UNDER 37 CFR 1.53

Attention: Box Missing Parts
Assistant Commissioner for Patents
Washington, D.C. 20231
Sir:

Enclosed is a Combined Declaration and Power of Attorney, executed by all of the inventors, to complete the subject application which was filed on September 27, 2001. Applicants are also enclosing at this time a certified translation of the Official Certificate of Inheritance for deceased inventor Thomas Scholl together with the Official Certificate.

01/28/2002 SECRETAR 00000082 09937998
01 FC:105 130.00 CP

Adjustment date: 03/12/2002 11:00:00
01/28/2002 SECRETAR 00000082 133848 09937998
01 FC:105 130.00 CR

03/12/2002 LLANDGRA 00000064 133848 09937998
01 FC:154 130.00 CH

Bayer sent 11/19/01

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231, on 11/19/01
Date
Noland J. Cheung, Reg. No. 39,138
Name of applicant, assignor or Registered Representative
[Signature]
Signature
November 19, 2001
Date

Copy of Declaration & Cert. of Inheritance enclosed here.

Hydroxyl group-containing solution rubbers

5 The present invention relates to rubber mixtures containing rubbers polymerised in solution with a secondary hydroxyl group content of 0.1 to 5 wt.%, which groups are no further than 4 carbon atoms away from the respective side chain end, and to their mixtures with fillers, optionally further rubbers and rubber auxiliary agents and vulcanisates produced therefrom. The rubber mixtures according to the invention are suitable for producing highly reinforced abrasion-resistant moulded articles, in particular for producing tyres which have a particularly high skid resistance in the wet and low rolling resistance.

10

Double-bond containing anionically polymerised solution rubbers, such as solution polybutadiene and solution styrene/butadiene rubbers have advantages over corresponding emulsion rubbers in the production of low rolling resistance tyre treads. The advantages are *inter alia* the controllability of the vinyl content and the glass transition temperature associated therewith and the molecular branching. These result in particular advantages in the relationship between skid resistance in the wet and rolling resistance of the tyre in practical application. Thus, US-A 5 227 425 describes the production of tyre treads from a solution SBR rubber and silica. To further improve the properties, numerous methods for end group modification have been developed, as described for example in EP-A 334 042, with dimethylaminopropyl acrylamide or, as described in EP-A 447 066, with silylethers. Owing to the high molecular weight of the rubbers the content by weight of the end group is low, however, and can therefore influence the interaction between filler and rubber molecule to only a small degree. It was an object of the present invention to produce solution SBR rubbers with a much higher content of active groups for filler interaction.

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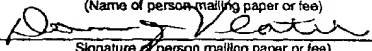
A further object of the present invention was the production of rubber vulcanisates with a more favourable skid resistance in the wet/rolling resistance relationship.

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Donna J. Veatch

(Name of person mailing paper or fee)


Signature of person mailing paper or fee

Hydroxyl group-containing solution polybutadiene rubbers are also described in DE-OS 2 653 144. However, these rubbers are not suitable as main components in tyre treads owing to their insufficient strength.

5 EP-A 464 478 describes a process for hydroxylation of rubbers, the hydroxylated rubbers differing structurally from those of the present invention. In particular, the secondary hydroxyl groups of EP-A 464 478 are located in a less favourable position in the polymer and are therefore far less effective than the hydroxyl groups of the present invention which are located no further than four carbon atoms away from the
10 respective side chain end.

EP-806 452 A1 also describes hydroxyl group-containing emulsion and solution rubbers, the hydroxyl proportions for solution rubbers described here lying in a much lower range (0.009 to 0.061 %) as a result of the process. The present patent applica-
15 tion shows that these proportions do not have any significant influence on the skid resistance in the wet and that the position of the hydroxyl groups is of particular importance.

The earlier applications DE-198 32 459.6 and DE-198 32 458.8 describe hydroxyl
20 group-containing solution rubbers. They do not, however, describe secondary hydroxyl groups and do not mention that the hydroxyl groups are located no more than 4 carbon atoms from the respective side chain end either.

It has now been found that rubber mixtures and rubber vulcanisates with surprisingly
25 improved dynamic cushioning properties in the temperature range (0 to 20 °C) relevant to skid resistance in the wet and in the temperature range (60 to 80 °C) relevant to rolling resistance and improved abrasion behaviour may be produced from hydroxyl group-containing solution vinyl aromatic/diolefin rubbers with a content of 0.1 to 5 wt.% bound secondary hydroxyl groups located no further than 4 carbon
30 atoms from the respective side chain end and with a 1,2 vinyl content of 5 to 60 wt.%. Further surprising advantages were obtained when the rubber mixture was produced

not in the kneader as is conventional, but by mixing a solution of hydroxyl group-containing rubber and oxidic or silicate-containing filler in organic solvent and subsequently removing the solvent with water vapour as the filler is then precipitated completely with the rubber and does not remain in the waste water, as is the case when using unmodified rubber.

The present invention therefore relates to rubber mixtures containing one or more hydroxyl group-containing rubbers polymerised in solution and synthesised from diolefins and vinyl aromatic monomers containing bound secondary hydroxyl groups in the range of 0.1 to 5 wt.%, characterised in that the secondary hydroxyl groups are located no further than 4 carbon atoms away from the respective side chain end. The invention also relates to the use of said rubber mixtures for producing rubber vulcanisates, in particular silica-filled tyre treads with particularly high abrasion resistance, particularly high skid resistance in the wet and low rolling resistance.

The vinyl aromatic/diolefin rubbers polymerised in solution advantageously have mean molecular weights (numerical average) of 50,000 to 2,000,000 and glass transition temperatures of -50° to +20°C.

Preferred proportions of vinyl aromatic are between 0.01 to 50 wt.%, particularly preferably between 5 to 40 wt.%.

Suitable vinyl aromatic monomers are styrene, o-, m- and p-methyl styrene, p-tert.butyl styrene, α -methyl styrene, vinyl naphthalene, divinyl benzene, trivinyl benzene and divinyl naphthalene. Styrene is particularly preferred.

Suitable diolefins are all diolefins known to the person skilled in the art, in particular 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene, 1-phenyl-1,3-butadiene and 1,3-hexadiene. 1,3-butadiene and isoprene are particularly preferred.

5 The rubbers according to the invention for the rubber mixtures according to the invention are preferably produced by anionic solution polymerisation, i.e. by means of a catalyst based on alkali metal, for example n-butyl lithium, in a hydrocarbon as solvent. The known randomisers and control agents can also be used for the micro-structure of the polymer. Such anionic solution polymerisations are known and described, for example, in I. Franta *Elastomers and Rubber Compounding Materials*; Elsevier 1989, page 73 to 74, 92 to 94 and in Houben-Weyl, *Methoden der Organischen Chemie*, Thieme Verlage, Stuttgart, 1987, Vol. E20, pages 114 to 134. The hydroxyl groups are introduced in a subsequent reaction to the final polymer. A preferred method for introducing hydroxyl groups is, for example, the addition of hydroxyl group-containing mercaptans.

10 Examples of suitable alkali metal polymerisation catalysts in the sense of the present invention are lithium, sodium, potassium, rubidium, caesium metal and their hydrocarbon compounds and complex compounds with polar organic compounds.

15 Lithium and sodium hydrocarbon compounds with 2 to 20 carbon atoms, for example ethyl lithium, n-propyl lithium, i-propyl lithium, n-butyl lithium, sec-butyl lithium, tert.-octyl lithium, n-decyl lithium, phenyl lithium, 2-naphthyl lithium, 2-butyl phenyl lithium, cyclohexyl lithium, 4-cyclopentyl lithium, 1,4-dilithiobut-2-ene, sodium naphthalene, sodium biphenyl, potassium-tetrahydrofuran complex, potassium-diethoxyethane complex, sodium-tetramethylethylene diamine complex are particularly preferred. The catalysts can be used alone or in a mixture.

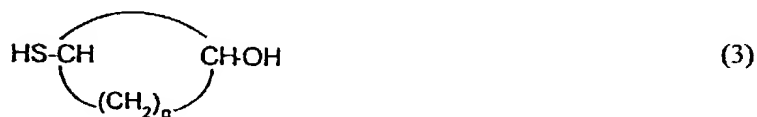
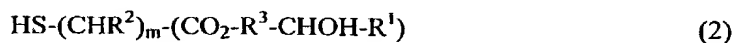
20 Preferred catalyst quantities are between 0.2 and 15 mMol/100 g of polymer.

25 The anionic solution polymerisation is carried out in a hydrocarbon or in another solvent which does not adversely affect the catalyst, for example tetrahydrofuran, tetrahydropyran or 1,4-dioxan. Hydrocarbons suitable as solvent are, for example, aliphatic, cycloaliphatic or aromatic hydrocarbons with 2 to 12 carbon atoms. Preferred solvents are propane, butane, pentane, hexane, cyclohexane, propene,

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butene, 1-pentene, 2-pentene, 1-hexene, 2-hexene, benzene, toluene, xylene. The solvents can be used alone or in a mixture.

The hydroxyl groups are preferably introduced by adding hydroxyl mercaptans of general formula (1), hydroxyl group-containing mercaptocarboxylic acid esters of general formula (2) and/or hydroxyl mercaptans (3). The reaction is preferably carried out in solution, optionally in the presence of radical starters.



wherein

R^1 represents a C_1 to C_3 -alkyl group, which can optionally bear further hydroxyl groups

R^2 represents hydrogen, a C_1 to C_6 -alkyl group or a $-\text{CO}_2 - \text{R}^3 - \text{CHOH} - \text{R}^1$ group and

R^3 represents a linear, branched or cyclic C_2 to C_{36} -alkyl group which can optionally be substituted by up to 6 further hydroxyl groups or can be interrupted by nitrogen, oxygen or sulphur atoms,

OH represents a secondary hydroxyl group,

n, m independently from one another represents an integer from 1 to 7,

q represents an integer in the range of 3 to 4.

Preferred hydroxyl mercaptans are 1-mercapto-2-propanol, 1-mercapto-2-butanol, 1-mercapto-3-butanol, 1-mercapto-2-pentanol, 1-mercapto-2-hydroxy-cyclohexane and 1-mercaptopropanediol. 1-mercapto-2-propanol, 1-mercapto-2-butanol, 1-mercapto-2-hydroxy-cyclohexane and 1-mercaptopropanediol (thioglycerol) are particularly preferred.

Preferred hydroxyl group-containing mercaptocarboxylic acid esters are monoesters of mercapto acetic acid, mercapto propionic acid, mercapto butyric acid and mercapto succinic acid with 1,2-propylene glycol, 1,2- and 1,3-butylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, glycerol, sorbitol. The corresponding esters of 3-mercapto propionic acid are particularly preferred.

Most particularly preferred are hydroxyl mercaptans and hydroxyl group-containing mercapto carboxylic acid esters which, in addition to the specific secondary hydroxyl group, bear a further hydroxyl group in the second or third position, such as thioglycerol.

Suitable radical starters for adding the hydroxyl mercaptans to the solution rubbers are, for example, azo initiators, such as azobisisobutyric acid nitrile, azobiscyclohexane nitrile and peroxides, such as dilauroyl peroxide, benzpinacols and benzpinacol silyl ether or photo initiators in the presence of visible or UV light. Particularly preferred are diacyl peroxides, in particular di-(3,3,5-trimethyl hexanoyl) peroxide, didecanoyl peroxide and dilauroyl peroxide.

Preferred quantities of radical starters are in the range of 0.5 to 20 wt.%, based on hydroxyl mercaptan.

The Mooney viscosity ML 1+4 of the copolymers is in the range of 10 to 200, preferably 30 to 150, measured at 100°C.

The content of polymerised 1,2-butadiene units ("vinyl content") is in the range of 5 and 60 wt.%, preferably 10 to 50 wt.%.

5 The content of polymerised vinyl aromatic is in the range of 0.01 to 40 wt.%, preferably of 5 to 40 wt.%, particularly preferably 10 to 30 wt.%.

10 The content of secondary hydroxyl groups is in the range of 0.1 to 5 wt.%, preferably in the range of 0.1 to 3 wt.%, particularly preferably in the range of 0.1 to 2 wt.%, most particularly preferably in the range of 0.1 to 1 wt.%, based on rubber.

15 The process according to the invention therefore allows targeted introduction of hydroxyl groups as a function of the desired removal from the side chain end.

20 The content of hydroxyl groups can be determined by known methods, in other words, for example by spectroscopy, titrimetry, elementary analysis or by determining the so-called hydroxyl value, in other words by reaction with reagents which eliminate titratable acids in contact with OH groups. See DIN 53 240 in this regard.

25 Of course, in addition to the specific secondary hydroxyl groups, which are no further than 4 carbon atoms away from the respective side chain end, the rubbers can also contain further functional groups, such as carboxylic acid and carboxylic acid ester groups.

30 The hydroxyl group-containing rubbers polymerised in solution can be used alone, in a blend with aromatic or aliphatic oils or in a mixture with other rubbers. In addition to natural rubber, synthetic rubbers are also suitable as additional rubbers for the production of rubber vulcanisates. Preferred synthetic rubbers are described, for example, in W. Hofmann, Kautschuktechnologie, Gentner Verlag, Stuttgart 1980 and I. Franta, Elastomers and Rubber Compounding Materials, Elsevier, Amsterdam 1989.

They comprise *inter alia*

- BR - polybutadiene
ABR - butadiene/acrylic acid-C₁ to C₄-alkyl ester-copolymers
CR - polychloroprene
IR - polyisoprene
5 SBR - styrene/butadiene rubber copolymers with styrene proportions of 1 to 60, preferably 20 to 50 wt.%
IIR - isobutylene/isoprene rubber copolymers
NBR - butadiene acrylonitrile rubber copolymers with acrylonitrile proportions of 5 to 60, preferably 10 to 40 wt.%
10 HNBR - partially hydrogenated or completely hydrogenated NBR rubber
EPDM - ethylene/propylene/diene copolymers

and mixtures of these rubbers. Natural rubber, emulsion SBR and solution SBR rubbers with a glass transition temperature above -50°C, which can optionally be
15 modified with silyl ethers or other functional groups, as described for example in EP-A-447 066, polybutadiene rubber with high 1,4-cis-content (> 90%), which is produced with catalysts based on Ni, Co, Ti or Nd, and polybutadiene rubber with a vinyl content of 0 to 75% and mixtures thereof are of particular interest for the production of motor vehicle tyres.

20 The rubber mixtures according to the invention contain 5 to 500 parts by weight of an active or inactive filler, such as

- highly dispersed silicas, produced, for example, by precipitating solutions of
25 silicates or flame hydrolysis of silicon halides with specific surface areas of 5 to 1,000, preferably 20 to 400 m²/g (BET surface area) and with primary particle sizes of 10 to 400 nm. The silicas can optionally also be present as mixed oxides with other metal oxides, such as Al-, Mg-, Ca-, Ba-, Zn-, Zr-, Ti-oxides,
30 -

- synthetic silicates, such as aluminium silicate, alkaline earth silicate such as magnesium silicate or calcium silicate, with BET surface areas of 20 to 400 m²/g and primary particle diameters of 10 to 400 nm,
- natural silicates, such as kaolin and other naturally occurring silicas,
- 5 - glass fibres and glass fibre products (mats, strands) or glass microbeads,
- metal oxides, such as zinc oxide, calcium oxide, magnesium oxide, aluminium oxide,
- metal carbonates, such as magnesium carbonate, calcium carbonate, zinc carbonate,
- 10 - metal hydroxides, such as aluminium hydroxide, magnesium hydroxide,
- carbon blacks. The carbon blacks to be used in this case are produced by the lamp black, furnace black or gas black process and have BET surface areas of 20 to 200 m²/g, such as SAF, ISAF, HAF, FEF or GPF carbon blacks.
- rubber gels, in particular those based on polybutadiene, butadiene/styrene
- 15 copolymers, butadiene/acrylonitrile copolymers and polychloroprene.

Highly dispersed silicas and carbon blacks are particularly preferred. The oxidic and silica fillers can be activated and/or hydrophobised with the known filler activators, in particular sulphur-containing silyl ethers and/or known hydrophobing agents.

The above-mentioned fillers can be used alone or in a mixture. In a particularly preferred embodiment the rubber mixtures contain a mixture of light fillers, such as highly dispersed silicas, and carbon blacks as filler, wherein the mixing ratio of light fillers to carbon blacks is 0.05 to 20, preferably 0.1 to 10.

The fillers are preferably added as solids or as suspension in water or a solvent to the solution of the hydroxyl group-containing rubber or rubbers polymerised in solution. The rubber solution can be produced in advance, but the solution originating from the polymerisation is preferably used directly. The solvent is subsequently removed

thermally or preferably with the aid of steam. The conditions of this stripping process may be easily determined by preliminary tests.

The fillers are also preferably added to the solid hydroxyl-group containing rubber or a mixture of rubbers and mixed in in a known manner, for example with a kneader.

The rubber mixtures according to the invention optionally also contain crosslinking agents. Sulphur or peroxides can be used as crosslinking agents, sulphur being particularly preferred. The rubber mixtures according to the invention can contain further rubber auxiliary products, such as reaction accelerators, antioxidants, heat stabilisers, light protection agents, anti-ozonants, processing aids, plasticisers, tackifiers, blowing agents, dyes, pigments, waxes, extenders, organic acids, retarders, metal oxides and activators such as triethanolamine, polyethylene glycol, trimethylol propane etc. which are known in the rubber industry.

In the preferred rubber mixtures with highly active precipitated silicas, use of additional filler activators is particularly advantageous. Preferred filler activators are sulphur-containing silyl ethers, in particular bis-(trialkoxysilyl-alkyl)-polysulphides, as described in DE 2 141 159 and DE-AS 2 255 577, oligomeric and/or polymeric sulphur-containing silyl ethers of DE-OS 4 435 311 and EP-A 670 347, mercaptoalkyltrialkoxysilanes, in particular mercaptopropyltriethoxysilane and thiocyanatoalkylsilylethers, as described, for example, in DE-OS 19 544 469.

The rubber auxiliary agents (see also J. Franta in *Elastomers and Rubber Compounding Materials*, Elsevier, 1989) are used in conventional quantities which depend *inter alia* on the intended application. Conventional quantities are, for example, quantities of 0.1 to 50 wt.%, based on rubber.

The rubber mixtures according to the invention are eminently suitable for producing moulded article of all kinds.

Non-limiting examples of these moulded articles are O-rings, profiles, seals, diaphragms, tyres, tyre treads, cushioning elements and tubes.

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Tyres and tyre treads are particularly preferred.

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Example 1

25 g 1-mercapto-2-propanol and 2 g azobiscyclohexane nitrile are added to a solution of 500 g solution SBR rubber Buna® VSL 5025-0 (Bayer AG, content of bound styrene 25 wt.%, content of 1,2-bound butadiene 50 wt.%) in 4 l of cyclohexane at 70°C. The mixture was then stirred for 16 hours at 80°C. 2.5 g of antioxidant Vulkanox® BKF (Bayer AG) were then added and the solvent distilled off with water vapour. After drying at 70°C under vacuum a colourless rubber with the glass transition temperature (DSC) of -6 °C and OH content of 0.9 wt.% was obtained.

Example 2

The process was carried out as in Example 1, using the following quantities:

500 g Buna® VSL 5025-0 (Bayer AG)

4 l cyclohexane

12.5 g 1-mercapto-2-propanol

1 g dilauroyl peroxide (as replacement for azobiscyclohexane nitrile) (Interlox LP, Peroxid Chemie, D)

Reaction temperature: 3 hours at 80°C. 2.5 g of antioxidant Vulkanox® 4020 (Bayer AG) were then added. A colourless rubber with a glass transition temperature of -13°C and an OH content of 0.45 wt.% was obtained.

Comparison examples

The process was carried out as in Example 1, using the following quantities:

| Comparison example | Solution SBR B. VSL 5025- 0 | Hydroxyl mercaptan | Radical starter and length of reaction | Glass transition temperature | OH content in the end product |
|-----------------------------------|-----------------------------------|---|--|------------------------------------|-------------------------------------|
| 1 | 500 g | 1.6 g 1-mercapto-2- ethanol | 0.2 g azobiscyclo- hexane nitrile 16 hours/80°C | -18°C | 0.07 wt.% |
| 2 (according to EP 464,478) | 500 g | 73.5 g 1-mercapto-2- hydroxy- dodecane | 1 g dilauroyl peroxide 3 hours/80 °C | -27°C | 1.0 wt.% |

Example 3

The following rubber mixtures (except for sulphur and accelerator) were produced at 140 ° to 150 °C in a 1.5 l kneader. Mixing duration in the kneader: 5 minutes. Sulphur and accelerator were subsequently added at approximately 50° to 70°C on a roller.

| Components | Comparison example 3.A | Comparison example 3.B | Comparison example 3.C | Example 3.1 according to the invention |
|---|------------------------------|------------------------------|------------------------------|--|
| Solution SBR rubber Buna® VSL 5025-0 (Bayer AG) | 70 | 0 | 0 | 0 |
| Rubber according to Example 1 | 0 | 0 | 0 | 70 |
| Rubber according to comparison Example 1 (EP 806 452) | 0 | 0 | 70 | 0 |
| Rubber according to comparison Example 2 (EP 464 478) | 0 | 70 | 0 | 0 |
| BR rubber Buna® CB25 (Bayer AG) | 30 | 30 | 30 | 30 |
| Silica Vulkasil® S (Bayer AG) | 70 | 70 | 70 | 70 |
| Aromatic mineral oil Enerthene 1849-1 (BP) | 37.5 | 37.5 | 37.5 | 37.5 |
| Silane Si 69 (Degussa) | 6 | 6 | 6 | 6 |
| Carbon black N 121 (Degussa) | 10 | 10 | 10 | 10 |
| Zinc oxide RS® (Bayer) | 2.5 | 2.5 | 2.5 | 2.5 |
| Stearic acid | 1 | 1 | 1 | 1 |
| Vulkanox® 4020 (Bayer) | 1 | 1 | 1 | 1 |
| Sulphur (Kali Chemie, D) | 1.5 | 1.5 | 1.5 | 1.5 |
| Vulkacit® CZ | 1/8 | 1.8 | 1.8 | 1.8 |
| Vulkacit® D | 2 | 2 | 2 | 2 |

The rubber mixtures were then vulcanised for 20 minutes at 170°C.

- 5 The vulcanisates had the following properties:

| Vulcanisate property | Comparison example 3.A | Comparison example 3.B | Comparison example 3.C | Example 3.1 according to the invention |
|---|------------------------------|------------------------------|------------------------------|--|
| Tensile strength (Mpa) ⁽¹⁾ | 14.6 | 16.3 | 14.6 | 12.6 |
| Elongation at break (%) ⁽¹⁾ | 390 | 380 | 380 | 275 |
| Modulus at 100 % elongation (Mpa) ⁽¹⁾ | 3 | 3 | 2.9 | 3.7 |
| Shore A hardness (23°C) ⁽²⁾ | 73 | 69 | 72 | 73 |
| Shore A hardness (70°C) ⁽²⁾ | 69 | 65 | 69 | 69 |
| Rebound resilience at 23°C (%) ⁽³⁾ | 28 | 28 | 28 | 22 |
| Rebound resilience at 70°C (%) ⁽³⁾ | 47 | 49 | 49 | 49 |
| Difference between the rebound resiliences at 23° and 70°C | 19 | 21 | 21 | 27 |
| Abrasion to DIN 53,516 (ccm) | 104 | 83 | 98 | 75 |

(1) determined by tensile test to DIN 52 504 with standard test piece 2

(2) determined to DIN 53 505

(3) determined to DIN 53 512

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The test results show that the properties of the rubber according to the invention with specific content and arrangement of the hydroxyl groups were improved with respect to the unmodified rubber (comparison 3.A), the rubbers with the same hydroxyl group content (1 wt.%, comparison 3.B) and with insufficient hydroxyl group content (0.07 wt.%, comparison 3.C). A much lower rebound resilience was measured at ambient temperature which, experience has shown, is accompanied by a considerable improvement in the skid resistance in the wet. The difference between the rebound resiliences at ambient temperature and 70°C is much greater in the rubber mixtures according to the invention, so the relationship of skid resistance in the wet and rolling resistance in the tyres is also much more favourable.

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Example 4

5 4.15 g thioglycerol (3-mercapto-1,2-propane diol) and 0.5 dilauroyl peroxide were added to a solution of 500 g solution rubber Buna VSL 5025-0 (Bayer AG) in 4 l cyclohexane at 80°C and stirred for 2 hours at 80°C. 2.5 g Vulkanox 4020 (antioxi-
dant from Bayer AG) were then added, the solvent distilled off with water vapour. After drying at 70°C under vacuum, 504.1 g of rubber with the viscosity ML 1 + 4 (100°C) 70 and an OH content of 0.26 wt.% were obtained.

10 **Example 5**

The following rubber mixtures (except for sulphur and accelerator) were produced at 140°C in a 1.5 l kneader. Mixing duration in the kneader: 5 minutes. Sulphur and
15 accelerator were subsequently added at approximately 50°C to 70°C on a roller.

| Components | Comparison | Example 5.1 |
|--|----------------|-------------------------------|
| | example 5.A | according to the invention |
| Solution SBR rubber Buna® VSL 5025-0 (Bayer AG) | 70 | 0 |
| Rubber according to Example 4 | 0 | 70 |
| BR rubber Buna® CB25 (Bayer AG) | 30 | 30 |
| Silica Vulkasil® S (Bayer AG) | 70 | 70 |
| Aromatic mineral oil | 37.5 | 37.5 |
| Enerthene 1849-1 (BP) | | |
| Silane Si 69 (Degussa) | 5.6 | 5.6 |
| Carbon black N 121 (Degussa) | 10 | 10 |
| Zinc oxide RS® (Bayer) | 3 | 3 |
| Stearic acid | 1 | 1 |
| Vulkanox® HS (Bayer) | 1 | 1 |
| Vulkanox® 4020 (Bayer) | 1 | 1 |
| Sulphur | 1.5 | 1.5 |
| Vulkacit® CZ | 1.8 | 1.8 |
| Vulkacit® D | 2 | 2 |

The rubber mixtures were then vulcanised for 20 minutes at 170°C.

- 5 The vulcanisates had the following properties:

| Vulcanisate property | Comparison | Example 5.1 |
|---|----------------|-------------------------------|
| | example 5.A | according to the invention |
| Tensile strength (Mpa) ⁽¹⁾ | 15.6 | 19.6 |
| Elongation at break (%) ⁽¹⁾ | 380 | 400 |
| Modulus at 100 % elongation (Mpa) ⁽¹⁾ | 1.8 | 1.4 |
| Shore A hardness (23°C) ⁽²⁾ | 72 | 65 |
| Shore A hardness (70°C) ⁽²⁾ | 69 | 65 |
| Rebound resilience at 23°C (%) ⁽³⁾ | 28 | 25 |
| Rebound resilience at 70°C (%) ⁽³⁾ | 46 | 50 |
| Difference between the rebound resiliences at 23° and 70°C | 22 | 25 |
| Tan delta 0°C | 0.387 | 0.562 |
| Tan delta 60°C | 0.153 | 0.11 |

(1) determined by tensile test to DIN 52 504 with standard test piece 2

(2) determined to DIN 53 505

(3) determined to DIN 53 512

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The test results show that the cushioning properties of the rubber according to the invention with specific content and arrangement of the hydroxyl groups were much improved with respect to the unmodified rubber (comparison 5.A). A much lower rebound resilience was measured at ambient temperature and a higher tan delta at 0°C which, experience has shown, are both accompanied by a considerable improvement in the skid resistance in the wet. The higher rebound resiliences at 70°C and the lower tan delta at 60°C of the rubber mixture according to the invention both show a lower rolling resistance with respect to the reference rubber mixture without the content of hydroxyl groups according to the invention. The difference between the rebound resiliences at ambient temperature and 70°C and between the tan delta values at 0 and 60°C is much greater in the rubber mixture according to the invention, so the relation-

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ship of skid resistance in the wet and rolling resistance in the tyres is also much more favourable.

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Claims

1. Rubber mixtures containing one or more hydroxyl group-containing rubbers polymerised in solution and synthesised from diolefins and vinyl aromatic monomers containing bound secondary hydroxyl groups in the range of 0.1 to 5 wt.%, characterised in that the secondary hydroxyl groups are located no further than 4 carbon atoms away from the respective side chain end.
2. Rubber mixtures according to claim 1, characterised in that the hydroxyl group-containing rubber or rubbers polymerised in solution have a content of polymerised vinyl aromatic in the range of 5 to 40 wt.% and a 1,2 vinyl content in the range of 5 to 60 wt.%.
3. Rubber mixtures according to claim 1, characterised in that styrene is used as vinyl aromatic monomer.
4. Rubber mixtures according to claim 1, characterised in that 1,3-butadiene and/or isoprene are used as diolefins.
5. Use of the rubber mixtures according to claim 1, for producing moulded articles of all kinds, in particular for producing tyre treads.

RUBBER COMPOSITIONS CONTAINING HYDROXYL GROUPS

ABSTRACT OF THE DISCLOSURE

The invention relates to rubber compounds that contain rubbers polymerized in solution with a secondary hydroxyl group content of 0.1 to 5 wt.-% that are not more than 4 carbon atoms away from the respective side chain end. The invention also relates to mixtures thereof with fillers, optionally additional rubbers and rubber auxiliary agents and the vulcanized rubbers produced thereof. The inventive rubber compounds are useful for producing highly reinforced, abrasion-resistant molded bodies, especially for producing tires that are characterized by excellent non-skid properties on wet surfaces.

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COMBINED DECLARATION AND POWER OF ATTORNEY

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

RUBBER COMPOSITIONS CONTAINING HYDROXYL GROUPS

the specification of which is attached hereto,

or was filed on March 20, 2000

as a PCT Application Serial No. PCT/EP00/02452

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 14 848.1
(Number)

Germany
(Country)

April 1, 1999
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

| (Application Serial No.) | (Filing Date) | (Status) |
|--------------------------|---------------|--------------------------------|
| | | (patented, pending, abandoned) |

| (Application Serial No.) | (Filing Date) | (Status) |
|--------------------------|---------------|--------------------------------|
| | | (patented, pending, abandoned) |

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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200210-012300

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